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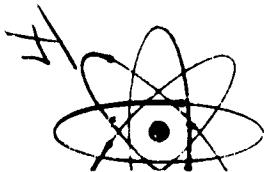
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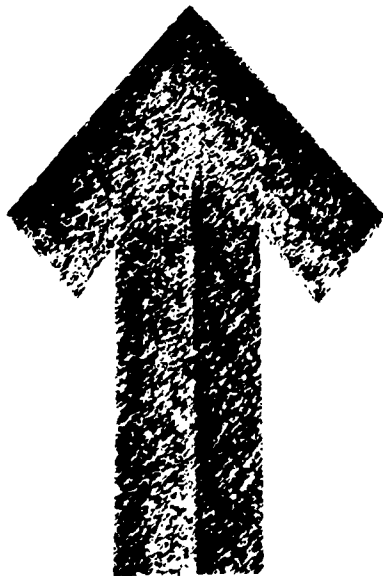
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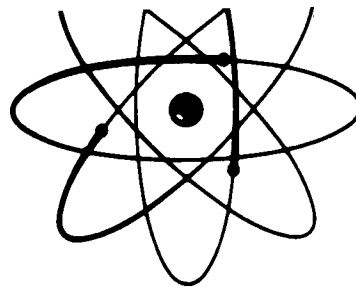
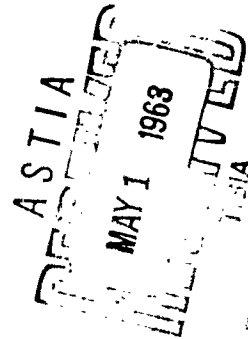
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Refractory Metals Phase Diagrams

Quarterly Progress Report

See this report

October 31, 1962 to December 31, 1962

E. J. Rappaport

Nuclear Metals, Inc.
Concord, Massachusetts

Contract No. AF33(616)-7137

This report has been reviewed and is approved

A. R. Rappaport
Technical Director

I. INTRODUCTION

This report summarizes the work performed on Contract No. AF33(616)-7137 during the fourth quarter (October 1, 1962 to December 31, 1962) of the current program in developing refractory metals phase diagrams.

The four participating laboratories, with their respective programs, are tabulated below:

Nuclear Metals, Inc.	MIT	MIT	Westinghouse Research Labs.
E. Rappaport	J. Brophy	B. Glessen	A. Taylor
Mo-Ti-Zr (also Mo corner of this system at several carbon levels less than 0.3%)	W-Pd Mo-Ir Cb-Ru Completion of Ta-W-Zr	Cb-Ir Cb-Rh	Cb-Hf W-Mo-Os W-Re-Hf

This program is a continuation of the study of refractory metal phase diagrams by four participating laboratories: Nuclear Metals, Inc., two groups at Massachusetts Institute of Technology, and Westinghouse Research Laboratories. Nuclear Metals, Inc., is acting as the prime contractor and manager of this program.

The quarterly progress reports for each participating laboratory are given below.

II. NUCLEAR METALS, INC. - E. Rappaport and V. Neres

In an effort to combat the serious segregation that has appeared in the melting of alloys in the system molybdenum-titanium-zirconium, a series of alloys were made by sintering powder compacts and then arc-melting the sintered products. Visual examination of twenty alloys prepared in this fashion revealed no segregation. An additional ten alloys previously made without the sintering step also showed no segregation with simple repeated arc-melting.

The successful fabrication of the difficult alloys was performed in the following fashion: Powders of pure molybdenum, zirconium hydride and titanium hydride were blended then reduced and sintered in vacuum by annealing the compacted powders for approximately 21-hours at 1425°C. The alloys were then arc-melted, turned over and remelted to a total of four melts on each side.

At the present time, some twenty-six alloys have been equilibrated at 1500°C for one week. Twelve of these twenty-six alloys were reported in the previous quarterly. The other fourteen are currently being prepared for metallographic examination.

The 1200°C equilibration has been run on five of the thirty alloys. These alloys were annealed for one week and are currently being prepared for metallographic examination.

Sight alloys in the two-phase field, molybdenum plus $ZrMo_2$, are being prepared with carbon contents of 0.1% and 0.2%. These alloys were chosen to be located relatively close to the α -phase boundary. The composition of these are as follows: Mo-20 a/o Zr, 5 a/o Ti; Mo-20 a/o Zr, 15 a/o Ti; Mo-20 a/o Zr, 20 a/o Ti; Mo-25 a/o Zr, 25 a/o Ti with each composition being made at the two carbon levels cited above. Weighted amounts of carbon (as lampblack or high purity graphite powder) will be added to molybdenum powder and well mixed. The mixed powders will then be cold-compacted and arc-melted without the addition of zirconium and titanium until after the arc-melting process. The effects of the carbon additions on the location of the two-phase boundaries will be ascertained utilizing the electron microbeam probe and x-ray lattice parameter measurements.

III. MASSACHUSETTS INSTITUTE OF TECHNOLOGY - J. Wulff and J. Brophy

During this report period the molybdenum-iridium diagram has been completed, the tantalum-tungsten-zirconium diagram is almost complete, and work has continued on niobium-ruthenium and tungsten-palladium.

A. Tantalum-Tungsten-Zirconium

In the tantalum-tungsten-zirconium system, recent results concern the component tantalum-zirconium binary, the ternary 1600°C isotherm, and the ternary solidus. In all of these studies the new vacuum furnace

chamber resulted in a vast improvement in alloy purity and accuracy of results.

New solidus measurements together with earlier diffusion couple results now confirm that the component tantalum-zirconium diagram shows a minimum melting point and solid state miscibility gap. These results differ slightly from a published version of the diagram (1) and will be reported more fully when complete. Resistivity measurements still place the eutectoid reaction at 785°C.

In the ternary system there appear to be two two-over-two four phase reactions. The reaction resulting from the alpha-beta transformation in zirconium lies between the eutectoids of the component binaries at about 800°C. Several low temperature cooling treatments are anticipated in the near future to locate the reaction more closely. The high temperature reaction involving liquid, beta zirconium, W_2Zr , and tantalum-tungsten rich solid solution occurs at 1760°C which lies between the eutectic in the tungsten-zirconium system and the minimum in the tantalum-zirconium system.

The 1600°C isotherm in the ternary system reveals solubility of two percent zirconium in alloys centrally located in the tantalum-tungsten binary. The W_2Zr compound extends into the ternary to approximately fifteen percent tantalum. The region of body-centered cubic zirconium is very small. A combination of lattice-parameters, electron microprobe examination, and quantitative metallography has been used to determine the 1600°C isotherm with surprisingly consistent results.

B. Molybdenum-Iridium

In the molybdenum-iridium system the completed diagram shows that the maximum solubility of iridium in molybdenum is sixteen atom percent at 2110°C but decreases to less than 5 atomic percent at 1500°C. Molybdenum dissolves into iridium up to 22 atom percent at 2200°C. Three intermediate phases appear in order of increasing iridium content: beta

(1) D. E. Williams, R. J. Jackson, W. L. Larsen: "The Tantalum-Zirconium Alloy System", Trans. Met. Soc. AIME, 224 (August 1962), p. 751.

(beta-tungsten structure), sigma, and epsilon (HCP). The beta phase exists between 22 and 25 atom percent iridium and from low temperatures up to a peritectic reaction at 2110°C. The sigma phase exists at 20 atom percent iridium, and decomposes peritectically at 2095°C and eutectoidally at 1975°C. The epsilon phase ranges from 37 atom percent iridium at 2080°C to 76 percent at 2300°C where it melts peritectically. The two phase region between HCP epsilon and FCC iridium rich solid solution is only two percent wide, but clearly evident metallographically and in X-ray patterns.

C. Niobium-Ruthenium

In the niobium-ruthenium system attention has been devoted to solidus measurements and metallographic techniques.

The solidus curve consists of a maximum at 1896°C and 50 atom percent ruthenium (mu phase) and a eutectic at $1733 \pm 10^\circ\text{C}$ and 65 atom percent ruthenium. On the low ruthenium side of the diagram there is a minimum in the solidus but at present it is not known whether this represents a eutectic or minimum melting point plus miscibility gap. Previous lattice parameter and diffusion couple measurements suggest a solid state miscibility gap below 1325°C. In this case, a continuous BCC phase above 1325°C becomes tetragonal upon cooling to produce the banded structure characteristic of the "mu phase".

D. Tungsten-Palladium

A series of solidus measurements in the region of tungsten solid solution plus palladium solid solution indicate a peritectic temperature of $1812 \pm 8^\circ\text{C}$. The composition of melted samples can be closely approximated from weight losses, but heat treated alloys must await fluorescent analysis. When a safe homogenization treatment is found, a series of alloy standards for wet analysis will be prepared.

The possibility of a minimum melting point in the palladium rich solid solution is under investigation. Raub and Walter⁽²⁾ reported melting below 1400°C. In our study a diffusion couple indicated a possible liquid region at 1500°C, but resistivity measurements revealed no irregularities up to 1450°C.

(2) K. Raub, P. Walters: "Alloys of the Platinum Group Metals with Tungsten," *Marneus Festschrift* (1951), p. 124.

IV. MASSACHUSETTS INSTITUTE OF TECHNOLOGY - N. J. Grant and B. C. Gleason

A. Niobium-Rhodium

The basis for the work in this period is the tentative diagram presented in the quarterly report July 1 - September 31, 1962.

Work on the Nb-rich and Rh-rich portions has been practically concluded and all major solvus lines and three phase reactions have been established. They are not repeated here, since no deviations other than quantitative ones from the lines given in the tentative diagram were encountered.

The center portion of the diagram has been treated again employing ground specimens for Debye-Scherrer X-ray work in an attempt to avoid the deformation and stacking faults introduced by powdering. From powder patterns the phase α_4 was unambiguously assigned the VCo_3 structure with a c/a ratio slightly deviating from the ideal value of $c/a = 2.450$. The next period will be devoted to outlining the other equilibrium phase fields in this region and calculating the unit cell lengths.

B. Niobium-Iridium

Work on this system was hampered in the last month by a necessary overhaul of the high temperature furnace and by the lack of a suitable refractory insulator for the Ir-rich alloys. This difficulty will now be overcome by the use of Ir wire, which makes it possible to suspend samples into the furnace without refractory oxide insulators.

The tentative diagram presented in the last quarterly report is regarded as essentially correct in the region from 0-50 atomic percent Ir, but will be substantiated by some additional measurements.

In the central region between 50-60 atomic percent Ir, there is some indication of an additional face-centered-tetragonal phase around 60 atomic percent Ir, analogous to that encountered in the Ta-Ir system; however, this will be worked out further in the next period.

The high Ir end of the diagram will be concluded on receipt of the Ir wire.

V. WESTINGHOUSE RESEARCH LABORATORIES - A. Taylor

A. Tungsten-Molybdenum-Osmium

new possible to construct a tentative constitution diagram of the W-Mo-Os system at 1600°C based on alloys homogenized at 2400°C for 2 days, lump annealed at 2000°C for 3 days, slow cooled over 24 hours to 1600°C and unannealed at 2000°C for 4 days, followed by radiation quenching. The diagram is shown in Fig. 1.

The precise location of the $\alpha + \beta + \gamma$ three-phase field needs to be established and a series of new alloys, indicated by the black dots has been made to fix its position. These are now being homogenized at 2400°C.

An interesting feature of the system is the position of the Mo₃Os β phase field, alloys of which have the so called β -W structure which is cubic. It would have been expected that the phase field would show a strong tendency to link up with the composition W₃Os along the line joining W₃Os to Mo₃Os. Actually the β -phase field starts at Mo₃Os but points toward 85 at.% Os on the W-Os edge, a composition which lies within the body-centered-cubic primary α W solid solution field at 2700°C.

B. Niobium-Hafnium

Heat treatments have been extended down to the 1250°C level for alloys containing 50 to 97.5 at.% Hf, and to 1080°C for an alloy at 40 at.% Hf. The X-ray and micrographic results obtained from these alloys has enabled the modified diagram to be constructed as shown in Fig. 2.

It would seem that the solid solubility limit of the close-packed hexagonal α Hf phase lies at approximately 98.5 at.% Hf at 1080°C. Visual examination of the X-ray diffraction patterns of α -phase alloys indicates that the lattice parameters of α Hf are increased quite substantially with Nb in solid solution. On the other hand, spacing measurements made in quenched body-centered-cubic β -Hf solid solutions indicates a reduction in size of the b.c.c. cell with Nb additions.

Traces of oxide are evident in the microstructures of Nb rich alloys containing up to 60 at.% Hf. A special alloy, using zone-refined Nb and iodide Hf has been made at the 50-50 at.% composition. This is presently undergoing homogenization at 2000°C.

C. Tungsten-Rhenium-Hafnium

Progress with this system has been slow owing to the difficulty of producing homogeneous alloys. Based on alloys which have now been satisfactorily homogenized and equilibrated, a tentative partial phase diagram for 2400°C has been constructed as shown in Fig. 3. The general outlines of the system would seem to be closely analogous to those of the system Mo-Re-Hf.

X-ray diffraction patterns and micrographs of γ -W₂Hf quenched at 2400°C indicate the presence of α W and β Hf phases. It would seem that the peritectic temperature of $2450 \pm 100^\circ\text{C}$ published by Grant et al. for the formation of W₂Hf is on the high side, and that it is probably in the region of 2350°C. It is intended to check this value in the next series of melting-point determinations.

END